

**UNCLASSIFIED**

**AD NUMBER**

**AD241309**

**LIMITATION CHANGES**

**TO:**

**Approved for public release; distribution is unlimited.**

**FROM:**

**Distribution authorized to U.S. Gov't. agencies and their contractors;  
Administrative/Operational Use; 10 JUL 1960.  
Other requests shall be referred to Army Signal Research and Development Laboratories, Fort Monmouth, NJ.**

**AUTHORITY**

**USAEC ltr dtd 17 May 1971**

**THIS PAGE IS UNCLASSIFIED**

**UNCLASSIFIED**

---

---

**AD 241309**

*Reproduced  
by the*

**ARMED SERVICES TECHNICAL INFORMATION AGENCY  
ARLINGTON HALL STATION  
ARLINGTON 12, VIRGINIA**



---

---

**UNCLASSIFIED**

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

241309

AD No.

ASTIA FILE COPY

SECOND TECHNICAL SUMMARY REPORT  
Report Date: July 10, 1960  
Period: Jan. 1, to June 30, 1960  
CONTRACT NR. DA-36-039-SC-85246  
Placed by  
U. S. ARMY SIGNAL RESEARCH &  
DEVELOPMENT LABORATORIES,  
FORT MONMOUTH, N.J.

6

**INVESTIGATION OF INTEGRALLY COMPOSED  
VARIABLE ENERGY GAP PHOTOVOLTAIC  
SOLAR ENERGY CONVERTER**

N-60-A-2

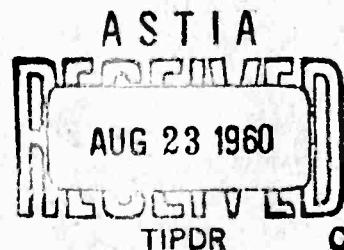
NOX



**THE EAGLE-PICHER RESEARCH LABORATORIES**

*Chemical & Metals Division*

*Miami, Oklahoma*



**SECOND TECHNICAL SUMMARY REPORT**

**Covering the Period**

**January 1, 1960 - June 30, 1960**

**Report Date: July 10, 1960**

**INVESTIGATION OF INTEGRALLY COMPOSED VARIABLE ENERGY GAP  
PHOTOVOLTAIC SOLAR ENERGY CONVERTER**

**ARPA Order Number 80-59**

**Date of Contract: September 1, 1959**

**Amount of Contract: \$35,740**

**Contract Number: DA-36-039-SC-85246**

**Report Prepared by:**

**L. E. Stone  
J. E. Powderly  
W. E. Medcalf**

**Report Edited by:**

**W. E. Medcalf**

**The Eagle-Picher Company  
Research Laboratories  
Miami, Oklahoma**

The work performed under this Contract was made possible by the support of the Advanced Research Projects Agency Order Nr. 80-59, through the U. S. Army Signal Research and Development Laboratory.

The Eagle-Picher Company  
Contract Nr. DA-36-039-SC-85246

TABLE OF CONTENTS

	<u>PAGE</u>
I. PURPOSE, . . . . .	1
II. ABSTRACT, . . . . .	2
III. PUBLICATIONS & CONFERENCES, . . . . .	3
IV. FACTUAL DATA	
Introduction, . . . . .	4
1. Fsbriication of Solar Cells, . . . . .	5
A. Materisls Used, . . . . .	5
B. Diffusion of Zinc, . . . . .	8
C. Diffusion of Phosphorus, . . . . .	10
D. Contacting, . . . . .	12
2. Evaluation of Solar Cells, . . . . .	14
A. Determination of Depths of p-n Junction, . . . . .	14
B. Junction Depth as a Function of Time & Tempersrure, .	19
C. Significance of Order of Diffusion of Zinc & Phos- phorus, . . . . .	20
D. Carrier Concentration, . . . . .	21
E. Detarmination of Phosphorus Diffusion Depth, . . . .	21
Transmission in Visibls & Infrared, . . . . .	22
F. Comparison of Single Gap & Variabla Gap Cells, . . .	26
G. Dark Diode Charactsristics, . . . . .	28
H. Summary of Data on Fabrication of Solar Cells, . . .	30
I. Conversion Efficiency at Maximum Power, . . . . .	31
V. CONCLUSIONS	
VI. PROGRAM FOR THE NEXT INTERVAL	
VII. PERSONNEL	

LIST OF TABLES & ILLUSTRATIONS

	<u>PAGE</u>
Figure 1. Single Crystals of Gallium Arsenide Growing in the (111) Direction, . . . . .	6
Figure 2. Single Crystal of Gallium Arsenide, cleaved to show (110) Face, . . . . .	6
Table I. Spectrographic & Electrical Data on Single Crystal GaAs, .	7
Figure 3. Schematic of Ambient Diffusion Furnace Using Electro- static Attraction, . . . . .	11
Figure 4. Variable Gap Cell Mounted for Testing, . . . . .	13
Table II. Etch Data, Single Gap Cell, Diffused with Zinc, . . . . .	15
Figure 5. Etch Time vs Diffusion Depth, . . . . .	17
Figure 6. Etch Time Short Circuit Current, . . . . .	17
Figure 7. Photomicrograph of Cell Surface, . . . . .	18
Table III Zinc Diffusion Depth in Gallium Arsenide as a Function of Time, Temperature and Ambient, . .	19
Table IV. Penetration of Zinc as a Function of Diffusion Sequence, .	20
Table V. Percent Transmission Values for Phosphorus Diffused Cells in the Range of 200 to 1020 Millimicrons, . . .	24
Figure 8. Transmission of Infrared in Phosphorus Diffused Cells, . .	25
Table VI. Comparison of Single Gap and Variable Gap Cells, . . . .	26
Table VII. Effect of Heat Treatment When Phosphorus Not Present, . .	27
Figure 9. Comparison of Increase in Voc and $I_{sc}$ After Diffusion with Phosphorus, . . . . .	28
Figure 10. Dark Diode Curves, . . . . .	29
Table VIII Statistical Comparison of Single Gap & Variable Gap Cells, . . . . .	30

1. PURPOSE

The purpose of the work on this Contract is to conduct an investigation of integrally composed multiple energy gap photovoltaic cells and to compare the characteristics of such cells with those of conventional single gap cells. The general objective is to increase the conversion efficiency above that obtained in single gap cells. The multiple band gap cell under study is a composite cell integrally composed of gallium arsenide and gallium phosphide. The first phase of the study consisted of developing the procedures of reproducibly fabricating gallium arsenide single gap cells. The second phase is the fabrication of the gallium arsenide-gallium phosphide cells and the carrying out of a comparative study of the two types of cells.

## II. ABSTRACT

A statistical comparison of 27 variable gap solar cells and 14 single gap cells fabricated during this work period indicated that the variable gap cells were superior to the single gap cells in (1) efficiency, (2) open circuit voltage, and (3) short circuit current. The average conversion efficiency and the maximum conversion efficiency in the case of variable gap cells were 4.08% and 6.9%, respectively, as compared with 2.43% average efficiency and 4.08% maximum efficiency in the single gap cells.

Several studies were carried out in which cells were made and evaluated as single gap cells, then diffused with phosphorus to form variable gap cells. Efficiencies, open circuit voltages, etc., invariably improved, even though the second diffusion resulted in deeper junction depths. A definite improvement in reverse current dark diode characteristics was noted in the variable gap cells with differences of an order of magnitude in the 5-volt region. Results, to date, have indicated that the sequence of diffusion giving best results is (1) diffusion of zinc followed by (2) diffusion of phosphorus.

An etching technique developed in the course of the work allows the determination of optimum junction depth for each cell. After etching to optimum junction depth, variable gap cells gave higher efficiencies than single gap cells similarly optimized. It is indicated that the p-n junction depth is less critical in the case of variable gap cells.

A consistent improvement in achieving purity and single crystal structure of the gallium arsenide crystals has resulted in improved and more reproducible solar cell fabrication.

### III. PUBLICATIONS AND CONFERENCES

During this period, letter reports were submitted on February 1, March 1, April 1, May 1, and June 1.

A Conference on Solar Cell Energy Converters was held on February 11, 1960 at Evans Laboratory, Fort Monmouth, New Jersey. Present were Mr. Cherry, Mr. Kesperis, Mr. Mandelkorn, Representatives from the Power Sources Group, and representatives from most of the ARPA sponsored research groups in the solar cell energy conversion field.

The Annual Power Sources Conference was held on May 17, at Atlantic City, New Jersey, and was attended by Mr. W.E. Medcalf and Mr. Louis Stone, of this Company. At this conference, a separate private conference was held with Mr. Cherry and Mr. Kesperis, of Evans Laboratory.

No publications have resulted from the research and development carried out thus far under this contract. It is planned, however, to present a paper on Integrally Composed Variable Gap Solar Cells at the A.R.S. Space Power Symposium, September 28, at Santa Monica, California. The paper will be based upon work carried out under this Contract.

IV. FACTUAL DATA

This section will be devoted primarily to experimental studies of the fabrication of two types of photovoltaic cells, (a) single band gap, and (b) variable band gap, and to the evalustion of their characteristics. A theoretical discussion of integrally composed variable gap cells was presented in the first technical report on this Contract and will not be further elaborated on here.

The single gap cells were prepared by diffusing p-type carriers such as cadmium or zinc into single crystal n-type gallium arsenide wafers to form a p-type diffused area at the surface of the crystal wafer approximately 1-micron deep. This ws followed by electroding and testing. The variable gap cells were made by the diffusion of phosphorus to varying depths in single crystal gallium arsenide wafers to provide a diffused area consisting of high concentration of gallium phosphide at the front surface of the crystal and gradually decreasing in concentration below the surface of the crystal thus providing a graded band gap approximately 2.2 ev at the surface to 1.35 ev in the interior of the cell.

The most important evaluation of the study was the comparison of the characteristics of the single gap and variable gap cells. These characteristics included open circuit voltage, short circuit current, saturation currents, dark diode characteristics and conversion efficiencies at maximum power output.

Important phases of the work were studies of techniques of (1) experimentally determining junction depth and boundary depth and determining the relative position of the junction depth and depth of phosphorus penetration. Other phases of the fabrication included the significance of separately or simultaneously diffusing phosphorus and p-type impurities and the sequence of such diffusions.

### 1. Fabrication of Solar Cells

#### A. Materials Used

The gallium arsenide single crystals were grown by three different procedures; (a) Czochralski technique, (b) Zone-levelling, and (c) a modified Bridgeman Technique with initial seeding of the melt with oriented crystals. The crystals grown by the latter procedure were more reproducible and proved more desirable for the fabrication of the solar cells. Most crystal growth was in the (111) direction. Figure 1 is a photograph of typical crystals grown by this technique. Figure 2 is a photograph of such a crystal cleaved on the (110) face. To date, no significant difference has been noted in the solar cell characteristics as a function of the orientation of the crystal. Table 1 lists spectrographic and electrical data on the gallium arsenide crystals used for fabricating the solar cells.



Figure 1. Single Crystals of Gallium Arsenide  
grown in (111) Direction.



Figure 2. Single Crystal of GaAs, cleaved  
to show the (110) Face.

**TABLE I. Spectrographic & Electrical Data on Single Crystal  
Gallium Arsenide**

Run Number	Description	Impurities (PPM)						Resistivity (ohm-cm)	Mobility (cm <sup>2</sup> /volt/se)
		Cu	Ca	Mg	Si	Pb	Fe		
G-2	Zone Refined,	.14	*	.04	*	1.2	*	13-2	3660
G-8	Zone Refined,	*	*	.05	*	*	*	2	6350
G-8A	Zone Refined,	.16	*	.07	*	*	*	----	----
G-9	Zone Refined,	.07	.09	.04	*	*	*	3.6 - 26.5	3000
G-10	Zone Refined,	.07	.086	.06	*	*	*	.05 - 6.25	----
G-12	Zone Refined,	.15	.02	.19	.36	*	.43	.019 - .61	4010
G-15	Zone Refined,	.6	.20	.207	.25	*	1.34	----	----
G-28	Modified Bridgeman,	.26	.36	.067	*	*	*	----	----
G-36	Modified Bridgeman,- doped with Sulfur,	---	---	---	---	---	---	.002	2600
G-37	Modified Bridgeman,	---	---	---	---	---	---	.1003	2600
G-38	Modified Bridgeman,	.16	.34	.62	*	.5	.34	.006	1620
G-39	Modified Bridgeman,	.44	.44	.12	*	.2	.47	.004 - .006	1740

(NOTE: \* = Not Detected)

Solar cells were fabricated from both zone refined and non-zone refined single crystal gallium arsenide with resistivities ranging from .001 to 10 ohm-centimeters. The most desirable resistivity range for solar cells has not yet been determined, but it is tentatively indicated to be between .01 and 1.0 ohm-centimeter.

B. Diffusion of Zinc

Two techniques for the diffusion of zinc were studied during the past work period. These were as follows: (a) Evacuated ampoule technique, and (b) diffusion at 1-atmosphere in ambient. A brief description of each follows:

(a). Evacuated Ampoule Technique

Wafers of GaAs are sawed from single crystal billets, lapped to rectangular shape and polished lightly with levigated alumina. They are then chemically polished and etched in HF-HNO<sub>3</sub>H<sub>2</sub>O 1:3:1 solution to give the clean polished surfaces desired. They are then placed in a clean quartz ampoule, on a clean quartz plate, with suitable dopant under the plate. The ampoule is flushed with helium and evacuated for five cycles, then sealed under vacuum. Diffusion for the desired time and temperature is carried out in quartz tubing 30 mm I.D., allowing accurate positioning and levelling. Following diffusion the ampoule is opened, the top surface masked with butyrate dope, the bottom surface lapped heavily to remove any "p" diffused material, and plated with electroless nickel. The edges are lapped heavily to remove "p" diffused material, and copper leads soldered to the nickel contact with 60-40 solder. The masking is then removed by solvents and the cell washed carefully with acetone, alcohol, and distilled water and weighed carefully. At this point, an etching process is normally carried out, by immersing in a dilute alkaline peroxide solution.

This etching procedure will be described in detail under the subject of determination of junction depth. Variable gap cells are processed similarly to the single gap cells, except for an additional diffusion step.

(b). Ambient Atmosphere Technique

Wafers, prepared as usual, are placed on a flat quartz plate in a 30 mm I.D. quartz tube and centered visually in a "split" furnace. A large amount (5 to 10 grams) of metallic dopant is placed in a quartz cup, welded to a quartz rod allowing it to be inserted and removed from the hot zone of the furnace. Helium is used to outgas for 30 minutes, at which time the gas flow is decreased, temperature raised to that desired, the dopant inserted into the hot zone and diffusion begun. After the desired interval, the dopant remaining is pulled outside the hot zone, effectively ending diffusion, helium bubbled slowly through the tube to remove any remaining metal vapor, and the cooling procedure begun.

Advantages of the open tube ambient technique include:

1. Elimination of staining and erosion incurred from residue after evaporation of moisture condensate produced during ampoule welding and,
2. Elimination of blue colored films or coatings on cell surfaces, tentatively identified as oxide coatings.

### Preferential Electrostatic Attraction

One of the inherent difficulties in the open tube method of diffusion is that of obtaining high carrier concentration. To overcome this difficulty, an attempt was made to increase the density of carrier concentration in the wafer surface by electrostatic attraction.

An electrostatic potential of 300 volts was placed on the wafers, and a potential of opposite polarity on a molybdenum plate directly above the wafers. The physical arrangement of the electrodes, wafers, etc., is shown schematically in Figure 3.

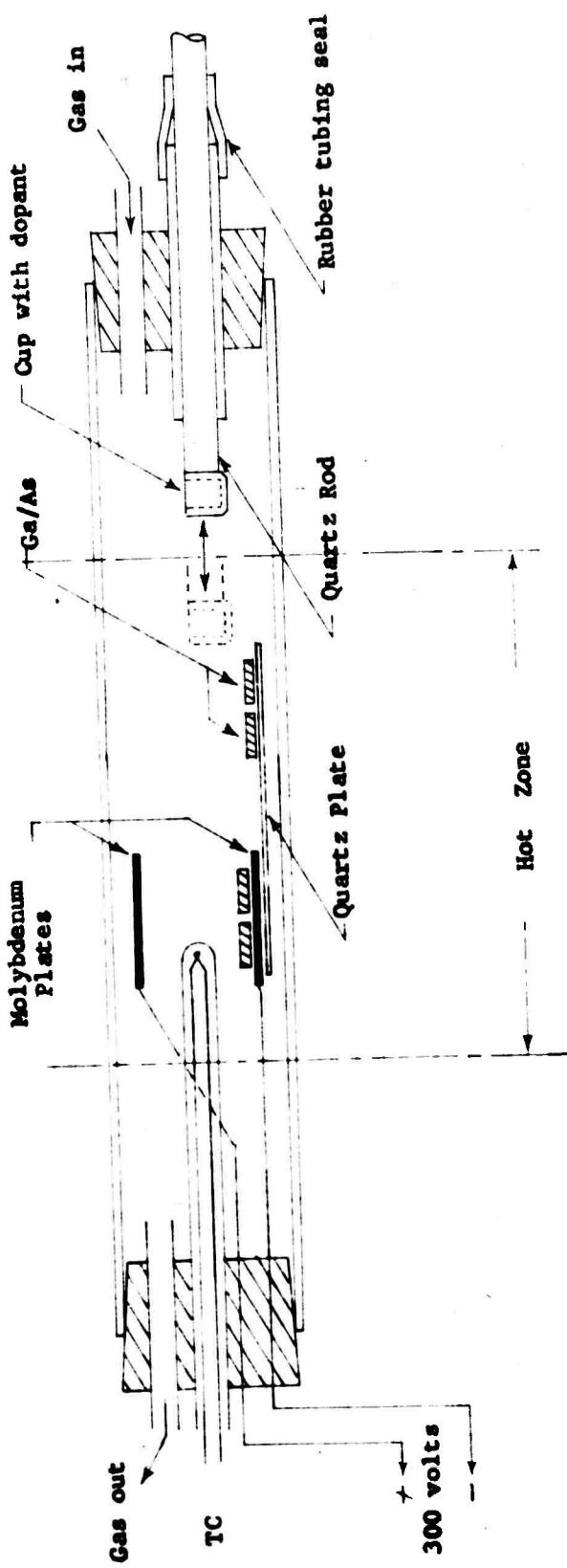
Results of diffusion studies on two wafers, to which an electrostatic potential was applied, showed increased zinc diffusion and diffusion to a greater depth. Two other wafers diffused simultaneously, but outside the applied field, had less zinc concentration by a factor of two. It was of interest to note that the molybdenum plates acted as an effective oxygen "getter" in addition to forming electrostatic electrodes.

### C. Diffusion of Phosphorus

Phosphorus diffusion, to date, has been by diffusion of elemental phosphorus in sealed, evacuated ampoules. Presence of Gallium Phosphide in rather high concentrations at the surface has been established by DeBya-Scherer X-ray studies.

FIGURE 3

Schematic of Ambient Diffusion Furnace Using  
Electrostatic Attraction



D. Contacting

(a). Ohmic contact to the bottom (N) surface of cells is made by plating with electroless nickel from an alkaline solution. This method supercedes the alloyed indium method, as we observed evidence of indium diffusion into the active surfaces of cells to their detriment. Masking during plating is done with butyrate dope, easily removed with solvents later. Considerable difficulty in plating n-type GaAs, and erratic contacting, was overcome by initiating the plating action by galvanic contact with iron in the form of wire. Once initiated, the iron contact is removed and normal plating continues very well.

(b) Collector contacting to top surface is done using silver paste. It is well known such a contact is considerably poorer than evaporated nickel contacts for example. However, in evaluating and comparing relative merits of single gap vs variable gap cells, it is believed use of the same cell for both forms makes perhaps the most valid of all comparisons. Hence, evaporated collector contacts, remaining on surface, would negate such comparison, due to single gap material under it, and difference in p-n junction geometry. Use of silver paste solves this difficulty nicely, bringing with it the disadvantage of contact resistance - about 1 to 5 ohms, a rather large value. This results in an effective loss in efficiency of up to one percent; i.e., a cell of 6% efficiency would check 5% or more, but the same relative loss is true for both forms of cells, hence allows relative comparison. For specific highest efficiency silver paste would not be acceptable.

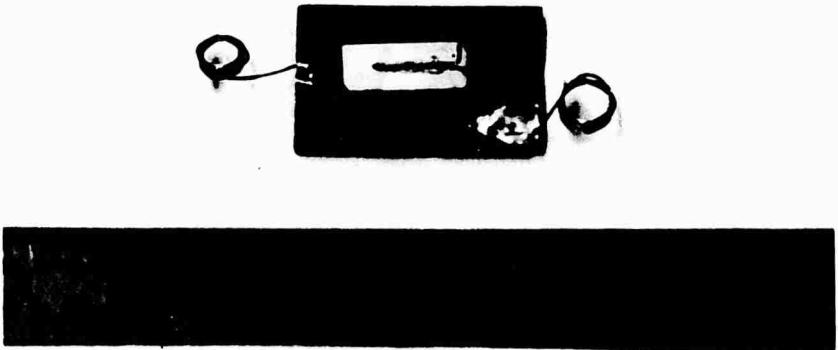


Figure 4. Variable Gap Cell Mounted for Testing

Illustrated above is a variable gap cell showing method of mounting on copper laminated board for testing purposes. Silver paste collector electrode is at center of cell surface. Copper wire leads are coiled at either side. Cell is shown approximately actual size.

## II. Evaluation of Solar Cells

### A. Determination of Depth of P-N Junction

There are several ways of determining the depth of diffusion of either cadmium or zinc in n-type gallium arsenide or in gallium phosphide/gallium arsenide wafers. These include (a) tracer techniques, and (b) 4-probe resistivity measurements. An accurate and very useful etching technique mentioned briefly under solar cell fabrication, has been developed in this laboratory and has been used to determine the junction depth and optimum junction depth with an accuracy not heretofore obtained. The procedure is carried out as follows:

After diffusion of the wafer and after the bottom surface of the wafer is plated with electroless nickel, a copper lead is soldered to the nickel and the wafer is rinsed in distilled water. The wafer is then dried, and placed under artificial light of about  $1 \text{ gm/cal/cm}^2/\text{min.}$  intensity. A pointed probe placed carefully on the surface of the cell is used to measure short circuit current and open circuit voltage. The diffused surface of the wafer is then carefully etched, using an alkaline peroxide etch ( $\text{KOH-H}_2\text{O}_2-\text{H}_2\text{O}$  1: 2: 5), and the procedure is repeated, with careful weighing each 15 seconds. At some point, a sharp rise in short circuit current under light will indicate the approach to optimum junction depth. Associated with the rise in current, will be a rise in open circuit voltage. The short circuit current will "level off" briefly, then decrease dramatically and sharply to zero as the effective junction is finally removed. Experience allows the optimum depth to be approached without "overshooting".

The cell is then carefully washed, and a silver paste-copper wire contact made to the upper surface, which is clean from the etching. Accurate measurements of the cell geometry and known specific gravity allow calculation of depth of surface removal. It is believed that the procedure provides accurate data on the effective junction depths and the optimum junction depth.

Table II provides typical data determined by using the above technique.

TABLE NO. II

Etch Data, Single Gap Cell, M6004 BN diffused Zinc 800°C, 60 minutes, Ambient Helium Atmosphere.

Time Seconds	Start	30	60	90	120	150	180	210	225	240
* $I_{sc}$	5 $\mu$ A	9 $\mu$ A <sup>a</sup>	14 $\mu$ A <sup>a</sup>	23 $\mu$ A <sup>a</sup>	47 $\mu$ A <sup>a</sup>	66 $\mu$ A <sup>a</sup>	.22 Ma	.32Ma	.30Ma	.50 $\mu$ A <sup>a</sup>
* $V_{oc}$ Volts	0	0	.1	.1	.1	.1	.16	.64	.65	.65
Weight grams	.3212	.3204	.3193	.3183	.3176	.3164	.3150	.3140	.3135	.3126
Microns Removed	0	2.3	5.15	7.7	9.5	12.5	16.2	18.7	20.0	22.3

NOTE: Cell L = .635 cm

\* Measured to point probe

W = .473 cm

Approximately 1 gm/cal/cm<sup>2</sup> Light.

T = .162 cm

The diffusion depth of zinc in GaAs single crystal wafers is shown in Figure 5. The graph also illustrates the time required for the etching as a function of depth of material removed from the wafer. Figure 6, on the same page, provides data on the change in  $I_{sc}$  as a function of etching time. It will be noted

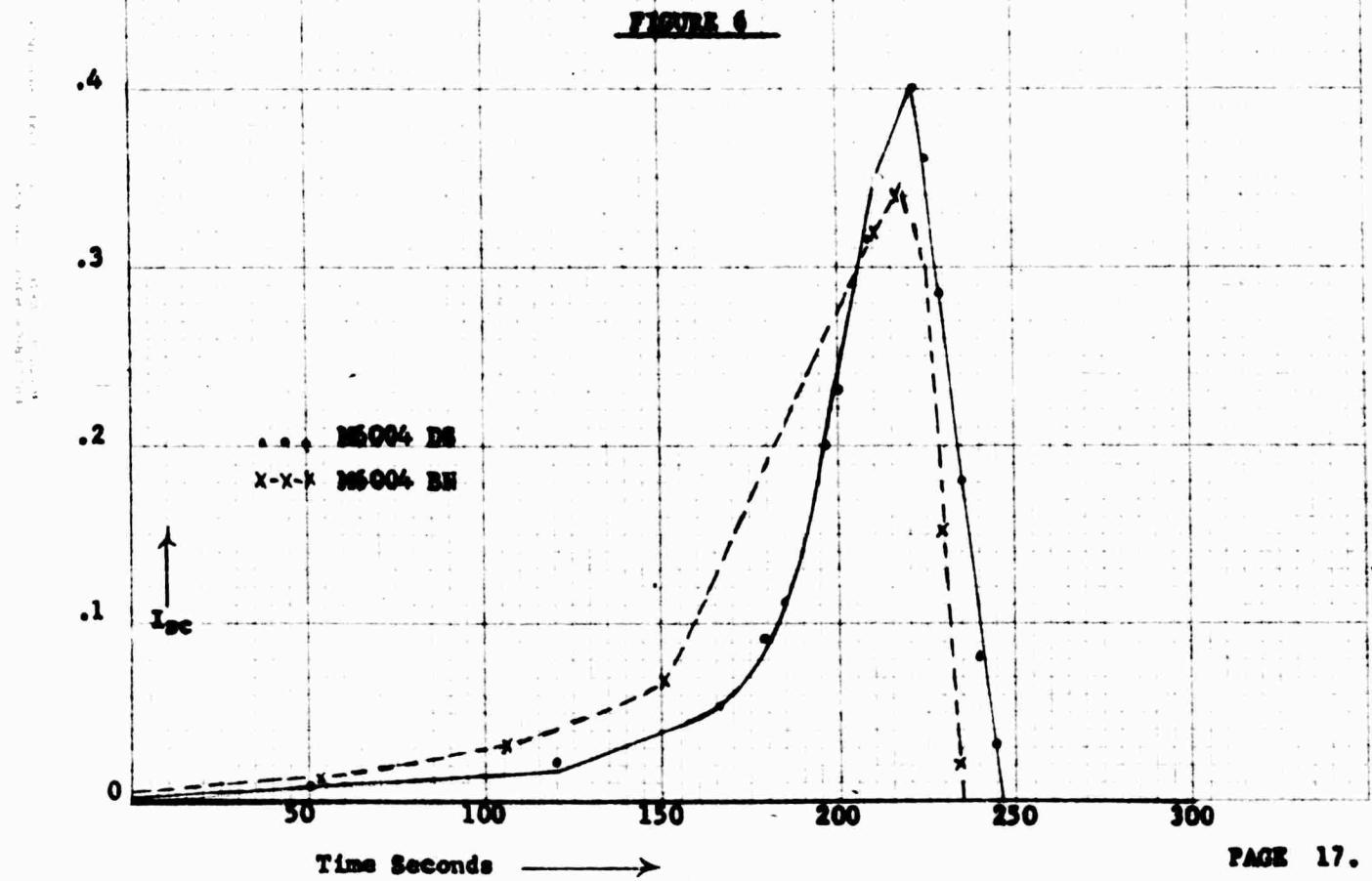
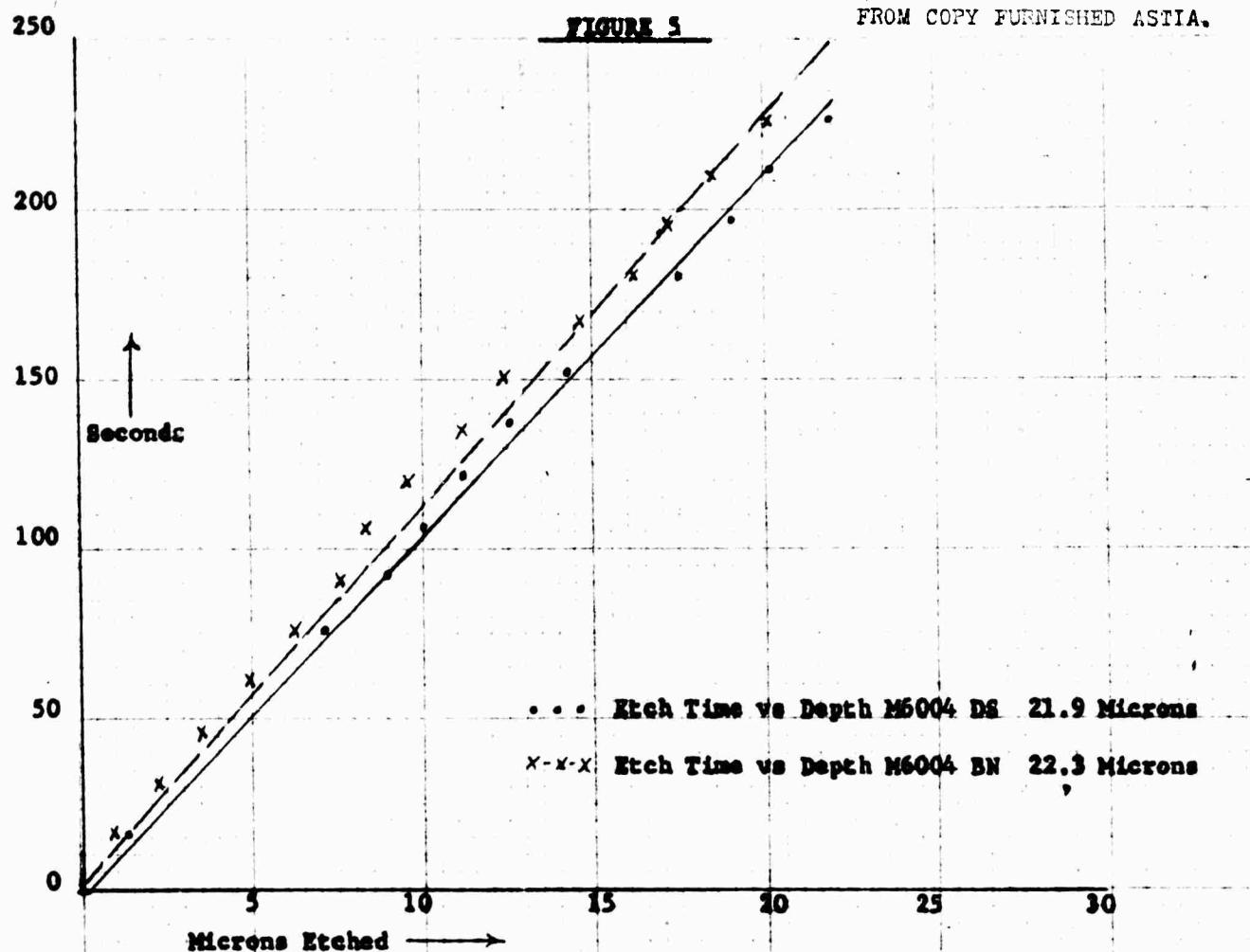
That the short circuit current increases rapidly with etching time and then falls quickly as the diffused area is finally removed. The short circuit current measurement here is to a point probe and is a relative factor only. The validity of this method assumes the following:

1. That etchant does not dissolve significant amount of the nickel ohmic contact, solder, or copper lead wire. This was checked by plating the entire surface of the wafer, soldering a copper lead as usual, and etching for 15 minutes in the standard solution. The total weight loss indicates a maximum error less than .5%, or accuracy better than 99.5%.

2. That area shrinkage does not significantly affect accuracy, since the total shrinkage in geometry is of the order of 20 microns or less, hence a second or third order of error.

Calculation based on this method gives a diffusion constant for zinc of  $7 \times 10^{-7} \text{ cm}^2/\text{sec.}$  @  $800^\circ\text{C}$ , which is in good agreement with known data, especially when it is recognized that the depth we measure is to the effective junction producing energy, rather than to the bottom of the compensated material. Value given in the literature is  $1 \times 10^{-6} \text{ cm}^2/\text{sec.}$  @  $800^\circ\text{C}$ .

Optimizing junction depth is routine to evaluation of cells. Good correlation has been obtained between diffusion time/temperature and optimum depth of junctions.



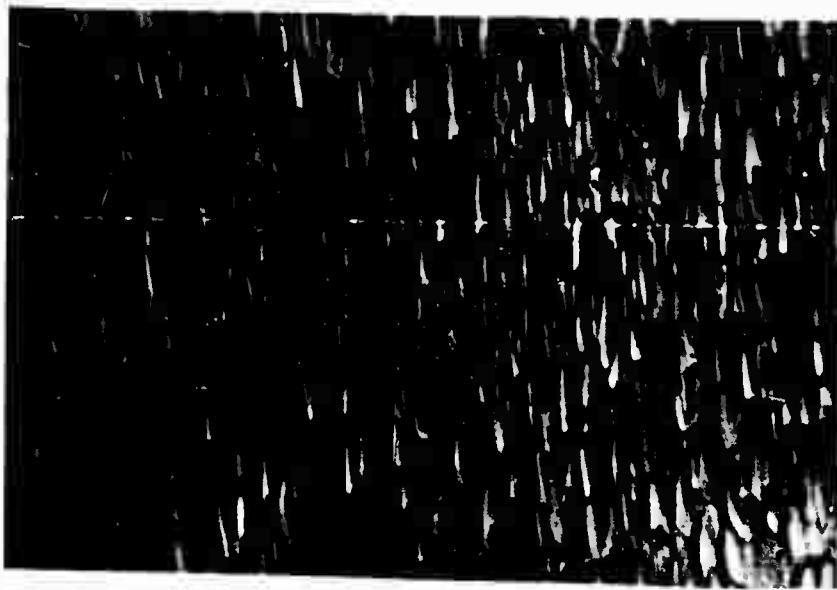


Figure 7. Photo-Micrograph of Cell Surface

Etched Surfaces of Cells

In as much as the alkaline peroxide etchant is known to be preferential in nature, it would be expected that etch pits or textured surfaces would be produced. Figure 7 is a photo-micrograph of such a textured surface, produced by etching a cell in the routine manner. The vertical height of the "hills" above the depressions range from .1 to .3 microns. This irregularity appears tolerable. It is believed any loss in conversion efficiency due to irregular depth of junction is partly or wholly overcome by increased utilization of reflected components of incident light. Further clarification of this effect will appear in the course of routine evaluation of cells.

B. Junction Depth as a Function of Time and Temperature

Table III below provides data on the depth of diffusion of zinc in gallium arsenide single crystal wafers as a function of time and temperature.

TABLE NO. III

Zinc Diffusion Depth in Gallium Arsenide as a Function of Time, Temperature and Ambient.

<u>Cell No.</u>	<u>Diffusion Schedule</u>	<u>Etch Time to Optimum</u>	<u>Microns Depth</u>	<u>Method</u>
Average of 6 cells,	Zn 750°C-30 Minutes,	30 seconds	About 2.5	Helium Atmosphere-Minimum dopant.
Average of 17 cells,	Zn 750°C-30 Minutes,	55 seconds	About 4.0	Evacuated Ampoule
Average of 11 cells,	Zn 750°C-30 Min., then Phos. 750°C-30 Minutes,	90 seconds	6.0	Evacuated Ampoule
Average of 8 cells,	Zn 800°C-30 Min., then Phos. 800°C-30 Minutes,	130 seconds	9.0	Evacuated Ampoule
Average of 3 cells,	Zn 750°C-60 Minutes,	220 seconds	About 15.0	Evacuated Ampoule
Average of 5 cells,	Zn 800°C-60 Minutes,	310 seconds	About 22.0	Evacuated Ampoule
Average of 2 cells,	Zn 800°C-60 Minutes - Preferential Electrostatic,	360 seconds	About 25.0	Helium Ambient, excess dopant.

C. Significance of Order of Diffusion of Zinc and Phosphorus

There is indication that when the phosphorus is diffused into the wafer before the zinc diffusion, the zinc penetration is more shallow. This may be due to a surface film formed during the diffusion, or from changes in atomic structure. Reference is made to Table IV, showing shallower penetration of zinc after phosphorus diffusion. Work on this phase is incomplete, but it is possible that this factor may be useful in limiting depth of P-N junctions. Tentatively, diffusion of the phosphorus before the diffusion of zinc, has resulted in lower carrier concentrations and lower efficiencies. This phase requires closer examination however before a definite comparison can be made.

TABLE NO. IV

Penetration of Zinc as a Function of Diffusion Sequence.

<u>Number of Cells</u>	<u>Diffusion Schedule</u>	<u>Average Etch Time to Optimum</u>	<u>Average Depth of Junction</u>
7 cells,	Phosphorus 750°C-30 Min., then Zinc 750°C-30 Min.	32 seconds	3 Microns
5 cells,	Phosphorus 800°C-120 Min., then Zinc 800°C-30 Min.	43 seconds	4 Microns
11 cells,	Zinc 750°C-30 Min., then Phosphorus 750°C-30 Min.	90 seconds	6 Microns
8 cells,	Zinc 800°C-30 Min., then Phosphorus 800°C-30 Min.	130 seconds	9 Microns

D. Carrier Concentration

Carrier concentrations are calculated from 4-probe resistivity measurements. Concentrations achieved to date have been considerably lower than optimum. They are further decreased after etching the surfaces. For this reason, work is in progress to obtain higher surface values, and shallower junctions. It is considered feasible that a final "flash" diffusion of zinc after achieving an optimum junction depth may produce the desired level of carrier concentrations without greatly impairing depth. Other techniques of either (1) high temperature with short diffusion time, or (2) low temperature with extremely long diffusion time are considered and some tentative efforts indicate either may be effective.

E. Determination of Phosphorus Diffusion Depth

Actual depth of the GaP boundary has proved difficult to establish. Microscopic identification of such a boundary using etch-stain techniques is possible, but difficult, and is not readily reproducible. Diffusion schedules, to date, have been based on the theoretical diffusion constant, and do offer some control. Some work using infra red transmission curves is being carried out, and offers some promise. It is considered that the use of a phosphorus glass for the source may give good control of phosphorus diffusion.

Transmission in Visible and Infrared

Studies were made of the transmission of light in the range of .2 to 1.0 micron and in the range of 3 to 15 microns. Three single crystal gallium arsenide wafers were studied. They were as follows:

<u>Reference Number</u>	<u>Sample Thickness</u>	<u>Description</u>
M6006 BZ	.25 mm	No diffusion
M6006 CA	.25 mm	Phosphorus diffused 30 Min. at 800°C.
M6006 CB	.25 mm	Phosphorus diffused 4 hours at 800°C.

It was hoped that there would be sufficient difference in transmission data that the process might be used as a tool to determine depth of phosphorus diffusion.

The results of the tests are shown in Table V and Figure 7. From Table V, it will be noted that there was no transmission below 900 millimicrons wavelength. From 900 millimicrons to 1020 millimicrons, there was no transmission in the specimen that was phosphorus diffused 4 hours at 800°C. There was .41 to 1.18 percent transmission in the sample diffused 30 minutes at 800°C, and .57 to 1.62 percent transmission in the sample which was not diffused with phosphorus.

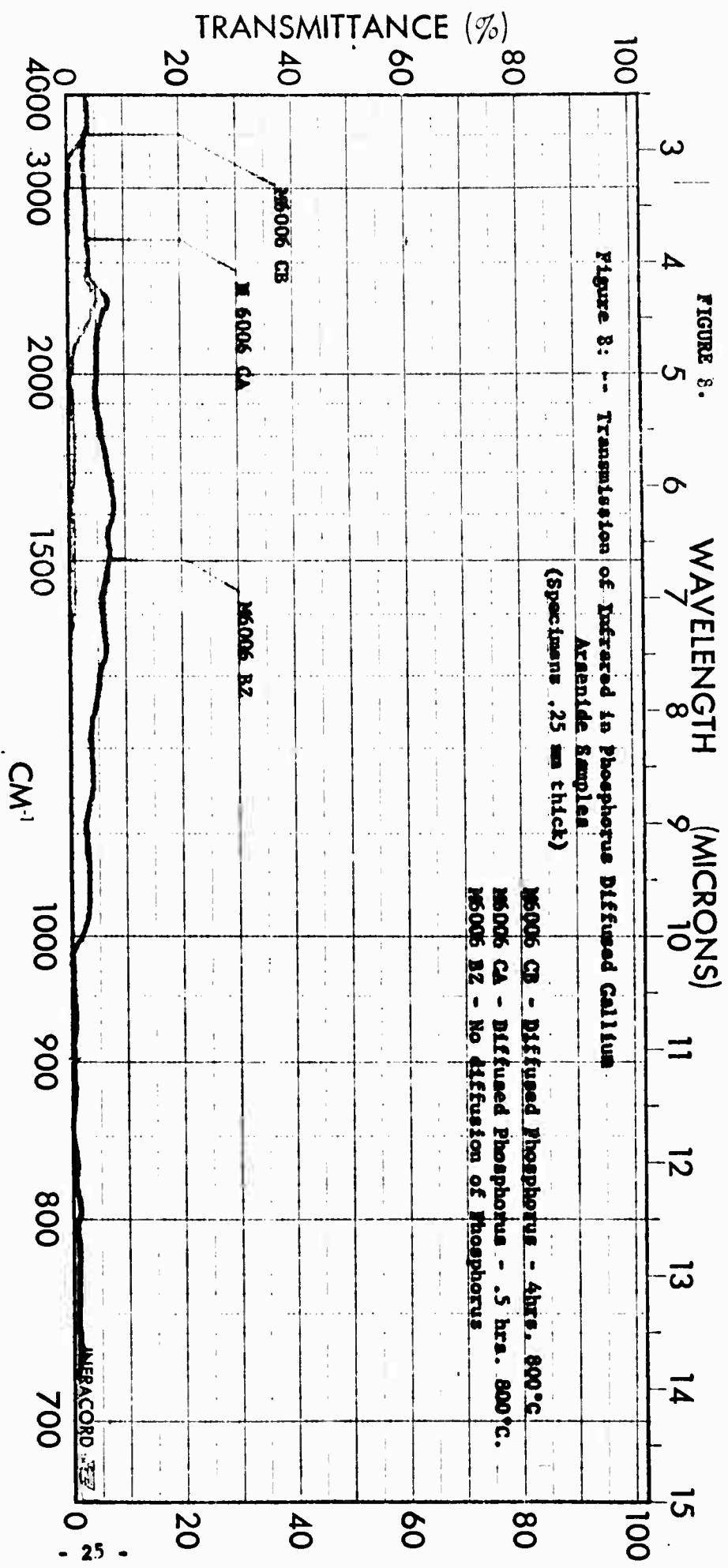
The infrared transmission is recorded in Figure 7. It will be noted that the transmission of infrared was greatest in the non-diffused sample and the lowest transmission was in the sample which was diffused the longest time - 4 hours at 800°C.

It is thus indicated that absorption is greater in the phosphorus diffused samples and greatest in the sample which was phosphorus diffused for the longest period of time. The transmission in all three samples was of a very low order. To obtain greater transmission and more significant differences, it is indicated that the specimens will need to have a smaller thickness. It will be difficult to lap the samples to a thickness that is less than .25 mm, but it may be possible by chemical etching.

TABLE NO. V

Percent Transmission Values for Phosphorus  
Diffused Cells in the Range of 200 to 1020  
Millimicrons.

Wave Length Milli-Microns	PERCENT TRANSMISSION		
	M6006 CB	M6006 CA	M6006 BZ
200	0	0	0
250	0	0	0
300	0	0	0
320	0	0	0
350	0	0	0
400	0	0	0
450	0	0	0
500	0	0	0
550	0	0	0
600	0	0	0
650	0	0	0
700	0	0	0
750	0	0	0
800	0	0	0
850	0	0	0
900	0	0	0
920	0	0.41	0.57
950	0	0.92	1.18
1000	0	1.5	1.62
1010	0	1.18	1.49
1020	0	1.15	1.29



F. Comparison of Single Gap and Variable Gap Cells

The indication of higher relative results with variable gap cells is substantiated by several studies in which cells were first fabricated and evaluated as single gap cells. After evaluation as single gap cells, the nickel contacts and silver electrodes were removed from the cells. The cells were then diffused with phosphorus. Results of such a representative study are illustrated by the following table.

TABLE NO. VI

<u>Cell Number</u>	<u>Percent Eff.</u>	<u>Voc.</u>	<u>I<sub>sc</sub>/cm<sup>2</sup></u>	<u>Approximate Junction Depth</u>
66, Single Gap,	.34	.31	1.85 Ma	2.5
Same, Variable Gap,	1.7?	.65	3.35	3.5
Same, Variable Gap etched to Optimum,	4.95	.73	9.7	Less than .5
67, Single Gap,	.43	.34	2.13	2.5
Same, Variable Gap,	1.41	.65	2.74	3.5
Same, etched to Optimum,	5.86	.73	11.4	Less than .5

The above data points up two factors as follows:

- (1). In each case the solar cell had improved characteristics after the diffusion of phosphorus, and
- (2). Each variable gap cell had improved characteristics after etching to secure optimum or nearly optimum junction depth.

To eliminate the possibility that heat treatment, as an annealing process, might be the significant factor in the improvement of the cell characteristics rather than the phosphorus diffusion, the following study was made: Four single gap solar cells of almost identical characteristics as cells #66 and #67, were sealed in an evacuated ampoule without phosphorus being present. The time-temperature processing was identical with that of the phosphorus diffusion cycle in the treatment of #66 and #67. The results are recorded in Table VII.

TABLE NO. VII

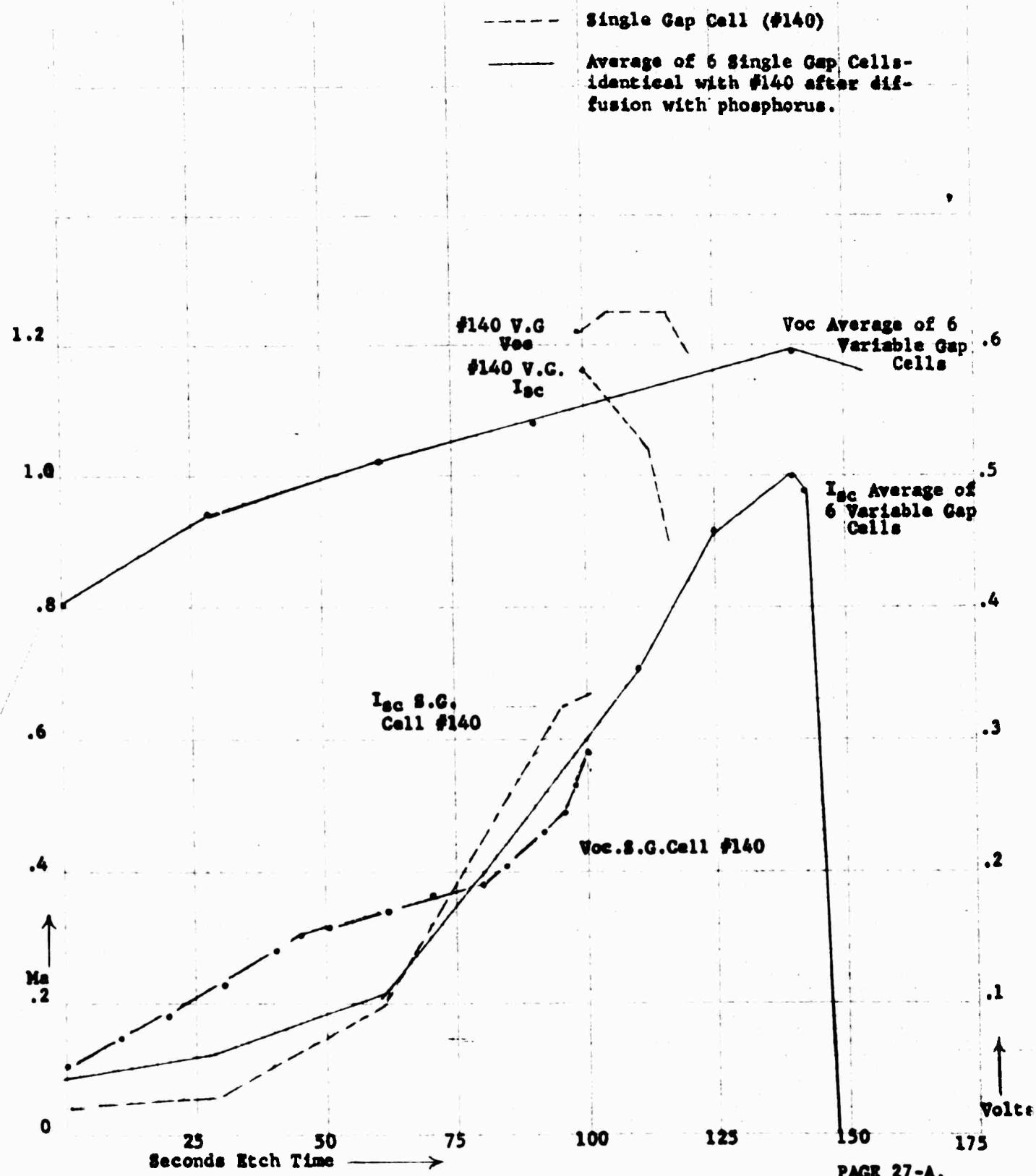
## Effect of Heat Treatment when Phosphorus Not Present

Cell	Percent Eff.	Voc.	$I_{sc}/cm^2$
72, Single Gap	.74%	.435	3.16 Ma
72, Heat Treated	.14	.235	.80
73, Single Gap	2.11	.60	10.0
73, Heat Treated	.46	.43	1.34
74, Single Gap	2.26	.61	6.64
74, Heat Treated	.88	.60	1.26
75, Single Gap	1.36	.40	5.13
75, Heat Treated	.1	.26	.51

The data provides evidence that the heat treatment or annealing was not the primary factor in the improvement of cell characteristics during phosphorus diffusion inasmuch as the heat treatment, when phosphorus was not present, caused significant deterioration of the cells. The decreased performance is believed due to increased junction depth and less sharp doping gradient at the junction.

In a similar study a group of five cells were fabricated as single gap cells. One of these, #140, was cut into two equal parts. Part "A" of this cell was etched to optimum junction depth, and its Voc and  $I_{sc}$  to a point probe recorded as shown in Figure 8. Maximum Voc was .3 volts, and  $I_{sc}$  was .66 Ma, and represent an efficiency of 1.5%. Part "A" was then diffused with phosphorus simultaneously with the remainder of the group. Part "A" then had a Voc of .62 volts, an  $I_{sc}$  of 1.16 Ma to a point probe. Full evaluation gave 4% efficiency. Part "A" was etched further, causing  $I_{sc}$  to decrease at once, indicating optimum junction depth in both cases. Part "B" and the remainder of the group were etched to optimum junction depth and evaluated. They had efficiencies greater than the single gap form of Part "A", but poorer than the variable gap form of Part "A". Figure 8 also illustrates the average of voltage and current rise of all six as variable gap cells.

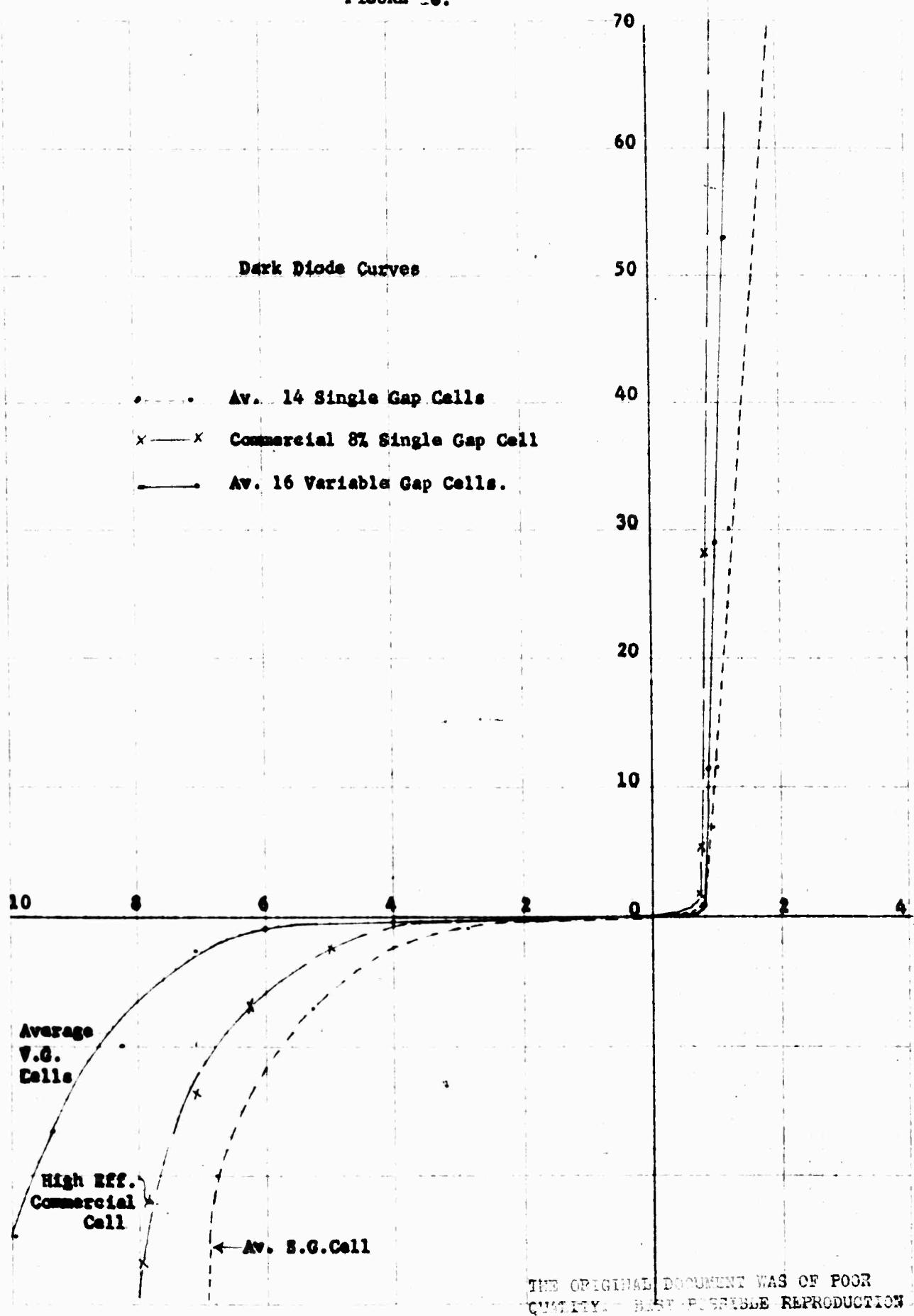
Figure 9



G. Dark Diode Characteristics

During evaluation of cells, it was noted that dark diode characteristics of Variable Gap cells exhibited better reverse current characteristics than Single Gap cells. The saturation current is known to decrease as the band gap of the semi-conductor increases, other parameters remaining constant. Investigation indicates approximately an order of magnitude improvement. Dark diode curves of sixteen variable gap cells and fourteen of the best single gap cells were averaged; the results are shown in Figure 9. Since it might be argued that the lower single gap efficiencies could reflect just such a parameter, a commercial single gap gallium arsenide cell was purchased and evaluated. This cell is considered to ably represent the present state of the art in single gap cells and checked 8% efficiency. Its reverse current characteristics is shown also in Figure 9. It is interesting to note that the average of the variable gap cells reverse currents is considerably less than this high efficiency single gap cell.

FIGURE 10.



H. Summary of Data on Solar Cells Fabricated During This Work Period

A total of 86 variable gap cells, and 30 single gap cells were made and evaluated this period. A statistical comparison of approximately half these cells in each case is best summarized by the following table. All cells were etched to optimum junction depth.

TABLE NO. VIII

Statistical Comparison of Single Gap and Variable Gap Cells

Cells	No. of Cells	Average Eff.	Maximum Eff.	Average Voc.	Maximum Voc.	Average Isc/cm <sup>2</sup>	Maximum Isc/cm <sup>2</sup>
Variable Gap,	26	4.68%	6.9%	.71 v.	.79 v.	10 Ma	15.2 Ma
Single Gap,	14	2.43	4.08	.63	.70	5 "	8.7 "

All cells included were fabricated the same, contacted the same, etc., in an effort to be as objective as possible statistically. It is believed that the comparison data on the single gap cells and the variable gap cells are significant. There is cognizance of the fact that single gap gallium arsenide cells of equal or higher efficiency have been reported.

## I. Conversion Efficiency at Maximum Power

The solar cells were evaluated under an RFL-2 lamp with an input power of 77 milliwatts  $\text{cm}^{-2}$  (1.1 cal/ $\text{cm}^2/\text{min}$ ).

The light had been calibrated with the sun at 1.1 cal/ $\text{cm}^2/\text{min}$  by the following method.

The short circuit current of a gallium arsenide solar cell ( $\text{Eff}_{\text{mp}} = 6.0\%$ ) was measured in the sunlight when the intensity was equal to 1.1 cal/ $\text{cm}^2/\text{min}$ . The short circuit current was measured several times and a mean value was recorded. The cell was then re-measured in the presence of the RFL-2 lamp and the intensity adjusted until the short circuit current duplicated the measured value in the sun. As a recheck, a different cell was measured both in the sunlight and artificial light. The artificial light is constantly rechecked for calibration both by the above technique and by a General Electric infrared meter.

As an additional check, a comparative evaluation of efficiency was made using a gallium arsenide cell prepared and evaluated by the Texas Instrument Company.

The above calibrations and measurements are accomplished with the light from the RFL-2 lamp filtered through approximately 1-inch of distilled water. It has been found that initial measurements with or without water are nearly the same if the light calibration is carefully considered. However, during a maximum power measurement (the light is on continuously) the cell which has not had the light filtered through water becomes warm and the true maximum power is not obtained.

The efficiencies at maximum power were determined by measuring the voltage across a variable load resistance which is in parallel with the photovoltaic cells. The maximum power is then calculated from the load voltage squared ( $V_L^2$ ) and divided by the load resistance ( $R_L$ ). The efficiency is determined by the following equation.

$$\text{Eff in \%} = \frac{\text{Output (milliwatts)} \times 100}{\text{Input (milliwatts)} \times \text{Area}}$$

V. Conclusions

A considerable amount of experimental data was obtained during the past work period which allows a definite conclusion that variable gap solar cells have definite advantages over single gap cells. Improvement in (1) conversion efficiencies, (2) open circuit voltages, and (3) short circuit currents were obtained in almost every case when diffusion of phosphorus into gallium arsenide was carried out under controlled conditions.

It is indicated that the sequence of diffusion providing the most desirable results are (1) diffusion of zinc or cadmium unto n-type gallium arsenide to provide a p-type diffused area followed by (2) diffusion of phosphorus. An etching technique developed to provide information as to the optimum p-n junction depth indicates that the junction depth for variable gap cells is less critical than in the case of single gap cells.

Difficulties recognized, and only partially solved, include (1) experimentally determining depth of phosphorus diffusion, (2) minimizing the sheet resistance, and (3) improving the lifetime in the diffused areas.

## VI. Program for the Next Interval

The following studies will be emphasized in the next work interval.

- (1). Location and control of depth of phosphorus diffusion
- (2). Concentration of phosphorus in the diffused area.
- (3). Spectral response studies of single gap and variable gap cells.
- (4). Sequence of diffusion of zinc and phosphorus.
- (5). Characteristics of variable gap cells as a function of purity, resistivity, mobility, lifetime and crystal structure of the gallium arsenide starting material.

VII. Personnel

Engineering Time Expended from 1 January to 30 June, 1960.

	<u>Hours</u>
W. E. Medcalf	168
L. E. Stone	1,024
J. E. Powderly	404
J. S. Roderique	168
Geo. N. Webb	704
Wm. A. Ames	195
Wm. J. Barlow	20
	2,683

UNCLASSIFIED

UNCLASSIFIED